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<p>Two diblock copolymers of polydimethylsiloxane and nylon 6 have been synthesized using a macromonomer approach. PDMS was synthesized anionically in THF and terminated with 11-(dimethylchlorosilyl)-N-undecanoyl-1-caprolactam, yielding a macromonomer capable of participating in the ring opening polymerization of caprolactam. This second step was carried out with $\text{LiAlH}_2(\text{OtBu})_2$ catalyst to activate the caprolactam monomer. Good yields and high molecular weight PDMS and Nylon 6 blocks were achieved.</p>					
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Syntheis of Poly(dimethylsiloxane) - Nylon 6 Diblock Copolymers

by

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SYNTHESIS OF POLY(DIMETHYLSILOXANE)-NYLON-6 DIBLOCK COPOLYMERS

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INTRODUCTION

Previous syntheses of polyamide-6 (PA6)-rubber block copolymers generally have used the macromonomer approach [1-6]. However, none of these pathways to di- and triblock PA6 copolymers has provided: 1) facile synthesis, 2) high PA6 molecular weights and 3) a chemical structure conducive to high temperature use. The poly(dimethylsiloxane) (PDMS)-PA6 diblock copolymers produced in this work via macromonomer chemistry have high PA6 molecular weights without unstable carbamate linkages which are the most common [3-6]. Thus, our PDMS-PA6 diblocks can be melt annealed at 250°C to generate simple morphologies which have been shown to possess improved mechanical toughness over homo-polyamide-6 [7].

EXPERIMENTAL

Coupling Agent Synthesis

The siloxane terminating/coupling agent was synthesized with slight modifications from Owen et al. [1]. Acylation of 10-undecenoylchloride with caprolactam (CPL) was done at 0°C in Et₂O with pyridine. The product was purified by filtration, washing with DI H₂O and drying with anhydrous MgSO₄. The 11-(dimethylchlorosilyl)-N-undecanoyl-1-caprolactam (DUC) was prepared by hydrosilylation of dimethylchlorosilane (DMCS, Petrarch) to N-10-undecenoyl-1-caprolactam catalyzed by hydrochloroplatinic acid (H₂PtCl₆·6H₂O) in THF at 25°C.

Polydimethylsiloxane Macromonomer Synthesis

The PDMS was synthesized anionically in THF (ca. 30 - 40 %w) by initiation of the cyclic trimer D_3 with n-BuLi at 25°C. Only several percent D_3 remained after 90 minutes as determined by size exclusion chromatography which indicated a polydispersity of 1.17. For one siloxane macromonomer, several percent of tetramethyltetravinylcyclotetrasiloxane ($D_{4\pi}$) was added sequentially to create a siloxane block copolymer of PDMS end-capped with a few $D_{4\pi}$ units. These could be used as complexing sites for heavy metal staining to give contrast in the electron microscope if desired.

The living siloxanolate was terminated with DUC and the reaction product filtered. The macromonomer was precipitated from THF with acetonitrile two times, dried and stored under argon. Molecular weights are detailed in Table 1.

Polyamide-6 Block Copolymerization

The initial nylon-6 catalyst, lithium caprolactamate, (LiCPL) was synthesized from freshly distilled CPL by reaction with n-BuLi under slight vacuum. The ring-opening polymerization of caprolactam proceeds by an activated monomer mechanism. Copolymerizations were always done in bulk under argon at temperatures above 150°C so that polyamide solubility was sufficient to reach high molecular weight [8]. The catalyst/initiator (C/I) ratio was maintained between 1.0 - 1.5 to minimize side reactions [9].

Due to the immiscibility between PDMS and CPL, mixing was accomplished via magnetic stirring or an ultrasonic dispersion horn (Rush Enterprises, Inc.). The latter was fitted with a 1/2" tip which produced ca. 75 watts of continuous waveform power and adapted to a Suslick cell via a special collar (Heat Systems, Inc.) designed for inert atmosphere. The cell was equipped with three 6 mm ports for introduction of reactants using hot, gas-tight syringes.

Copolymer MSN(3/100) [10] was synthesized using LiCPL catalyst, 170°C and magnetic stirring. USMSN(15/44) was synthesized using a novel coordinating catalyst at 155°C with ultrasonic dispersion. Workup consisted of dispersing the products in 2,2,2-trifluoroethanol (TFEtOH) and precipitating into THF two times followed by drying in vacuo. The final copolymers were analyzed by SEC as described elsewhere [11] and by solution ^1H ($\text{d}_2\text{-HFIP}$) and solid state ^{13}C NMR.

RESULTS AND DISCUSSION

The ^1H NMR spectrum for copolymer MSN(3/100) is shown in Figure 1a; similar ratios of peak areas were obtained by ^{13}C solid state NMR (not shown). Combined with data from SEC, the average molecular weight of the siloxane block in the copolymer was determined to be only 3 kg/mole versus its original $\bar{M}_n = 10.5$ kg/mole; the PA6 block \bar{M}_n reached 96 kg/mole (Table 1). ^1H NMR of the filtrate (THF phase) showed significant amount of siloxane indicating either poor conversion of the ω -N-acyllactam groups or siloxane depolymerization.

Chemical Stability of Siloxane to Caprolactam/Catalyst

Due to the large amount of siloxane in the filtrate of MSN(3/100), the stability of PDMS to CPL and catalyst was examined by "simulation polymerizations". These experiments consisted of mixing ordinary trimethylsilyl-terminated PDMS in CPL and catalyst at various temperatures and measuring the PDMS molecular weight distribution (MWD) via SEC as a function of time. It should be noted that PDMS is stable to CPL (alone) at 170°C for 24 hours. However, when LiCPL was added to PDMS/CPL, significant depolymerization occurred as shown in Figure 2. The dashed curve represents the original MWD, the dot-dashed curve corresponds to the PDMS MWD after 65 minutes at 90°C with 1.5 C/I ratio, and the solid curve represents the PDMS MWD after 65 minutes exposure to

1.5 C/I at 170°C, the temperature for MSN(3/100) copolymerization. Thus, significant depolymerization of PDMS evidently occurred during formation of the PA6 block of MSN(3/100).

Additional "simulation polymerization" experiments were conducted with LiAlH_4 catalyst. If toluene solution polymerization was simulated at 110°C following ref [1], then no depolymerization of PDMS occurred; however as mentioned above these conditions lead to low PA6 block molecular weights. However, if the temperature is raised to 153°C in bulk, ca. 35% of the PDMS is depolymerized to cyclics (D_3, D_4) after 120 minutes with LiAlH_4 .

Synthesis Improvements for PA-6 Block

In order to synthesize high molecular weight PA6 blocks, bulk conditions and higher polymerization temperatures are necessary. But as seen above, significant PDMS depolymerization occurs with traditional catalysts. Therefore, new catalysts were needed that reduce the nucleophilicity of the lactam anion but do not interfere with the activated monomer mechanism. This was accomplished through the synthesis of derivatized LiAlH_4 , e.g. $\text{LiAlH}_2(\text{OtBu})_2$, catalysts which markedly improved the chemical stability of PDMS. As seen in Figure 3, this new catalyst resulted in only a slight broadening in the MWD after 2 hours at 153°C, with no cyclics generation; yet upon introduction of an N-acyllactam moiety, CPL polymerization commenced immediately with little loss of activity.

These new catalysts combined with ultrasonic dispersion improved the siloxane viability and yield. Shown in Figure 1b is the ^1H NMR spectrum of USMSN(15/44) after workup; a much larger methylsilyl proton peak near 0.07 ppm is evident. SEC analysis of the THF filtrate shows only linear, unreacted siloxane and no cyclics. The higher yield of PDMS for USMSN(15/44) versus MSN(15/44) is reflected in the better mixing and more viable catalysts.

Conversely, the higher polymerization temperatures for MSN(3/100) are responsible for the higher conversion of CPL due to increased solubility of the polyamide in CPL. See Table 1 for details.

For USMSN(15/44), it took approximately 4 hours to convert the entire 10 cm³ volume into solid copolymer yet roughly half of the CPL was unreacted (which is not representative of equilibrium conversion). This was due to the reduced basicity of the new catalysts and the fairly low reaction temperature. The latter slowly caused precipitation of the reactive PA6 anions out of the melt further reducing the basicity (or rate). This precipitation, combined with a strong thermal driving force for crystallization eventually stopped the copolymerization prematurely.

The morphology of this USMSN(15/44) diblock, which is presented elsewhere [7], shows fairly uniform PDMS spheres with a diameter of ca. 250 Å micellized in a matrix of PA6.

CONCLUSIONS

The development of a coordinating catalyst that reduces the nucleophilicity of the caprolactam anion has permitted the successful anionic copolymerization of CPL by a PDMS macromonomer. The new catalyst eliminates the depolymerization of PDMS in bulk caused by earlier catalysts, such as LiCPL or LiAlH₄.

Ultrasonic mixing has significantly reduced the siloxane droplet size and improved the accessibility of the ω -N-acyllactam to the catalyst. With smaller droplets, more imide groups are able to diffuse to or locate at the interface and increase PDMS conversion into copolymer.

This methodology yields reasonably monodisperse diblock copolymers of PDMS and PA6 that have increased toughness over homo-PA6. Future efforts will be

focused on copolymerizing PDMS (and other siloxanes) at higher temperatures and C/I ratios to improve CPL conversion and rate of reaction as well as exploring alternate lactam copolymers from nylon-4 to nylon-12.

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8. O. Wichterle, *Makromol. Chem.*, **35**, 174 (1960).
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10. Nomenclature: MSN = methylsiloxane-nylon-6 diblock copolymer; US = ultra-sonic; numbers represent block \bar{M}_n .
11. C.A. Veith and R.E. Cohen, *Polymer*, **30**, 942 (1989).

TABLE 1
PDMS-PA6 COPOLYMERIZATION DATA[†]

Polymer	PDMS		Diblock [‡]		Comp. PDMS	% Yield	Percent Conversion	
	\bar{M}_w	PDI	\bar{M}_w	PDI	wt% / mol%		PDMS	PA6
MSN	12.3*	1.17	133	1.34	2.9 / 4.3	60.3	9.6	71.6
USMSN	17.6	1.20	96	1.66	25.4 / 34.1	35.3	55.3	31.3

* Initial PDMS block \bar{M}_w in kg/mole;

[†] PDI = polydispersity index; yield = g MSN + total g in

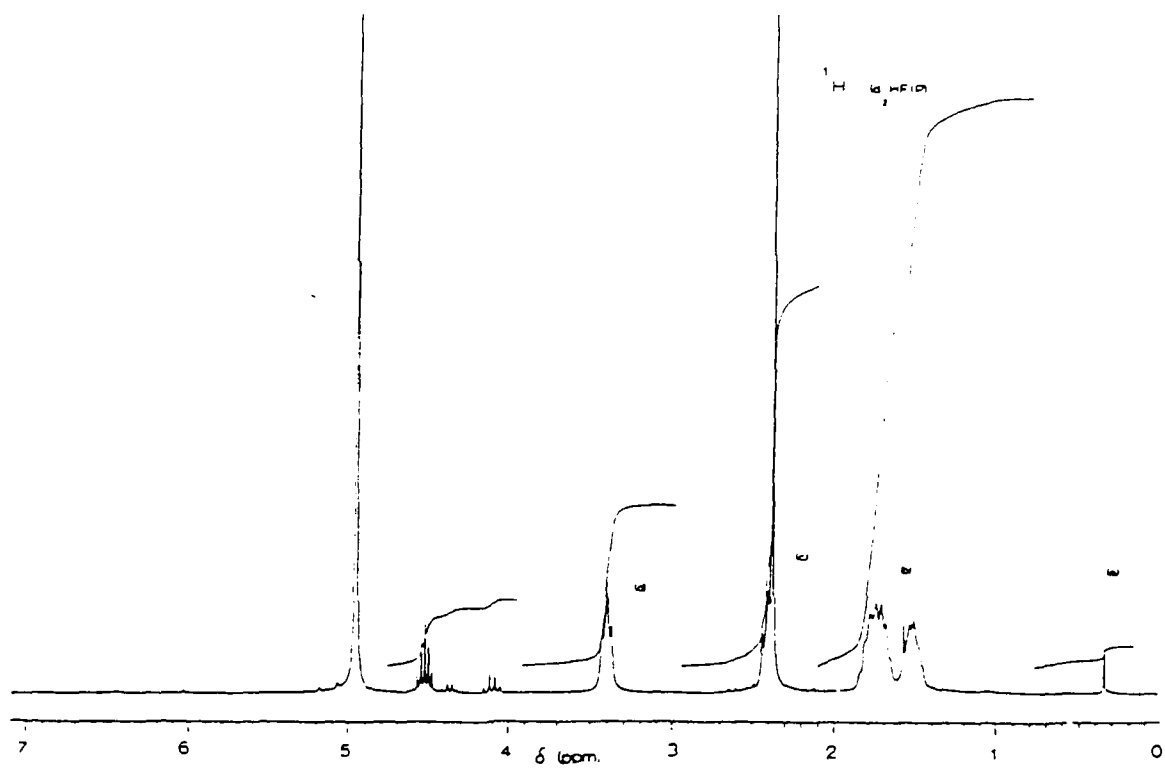
[‡] From nylon-6 SEC calibration; ref [11].

Figure 1: ^1H NMR for a) MSN(3/100), b) USMSN(15/44).

Figure 2: MWD of PDMS in CPL and LiCPL via SEC

Figure 3: MWD of PDMS / CPL / coordinating catalyst mixture.

(a) NMR PDMS-NYLON6 DIBLOCK COPOLYMER



(b)

